(54) Title: DIARYLACETYLENES, ENAMINES AND ACETYLENIC POLYMERS AND THEIR PRODUCTION

(57) Abstract

    Diarylacetylenes and diarylenamines are synthesized from a Schiff's base and an N-arylmethylheterocycle; these com-
pounds are useful as intermediates for a variety of polymers; in particular an efficient process is provided for producing diaryl
acetylenes useful in the efficient production of acetylene group-containing polymers which can be cross-linked to produce high
strength polymers free of structural defects such as conventionally arise as a result of liberation of volatiles during the cross-link-
ing.

DIARYLACETYLENES, ENAMINES AND ACETYLENIC
POLYMERS AND THEIR PRODUCTION

TECHNICAL FIELD

This invention relates to processes for
producing diarylacetylenes and enamines which are
valuable in the synthesis of homopolymers and copoly-
mers, for example, poly(arylether)s, polyesters,
polycarbonates and polyformals.

BACKGROUND ART

Advanced composite materials are made from
combinations of high performance fibers, such as
glass, graphite, carbon, silicon carbide or ceramic
fibers, arranged in close packed alignment in the
polymer as a matrix. Such composite materials
provide a combination of strength and modulus sup-
erior to that of structural metals and alloys on an
equal weight basis. Such composites are, for
example, employed in military and commercial air-
craft, and space vehicles, as well as in sports
equipment, in tennis racquets, shafts for golf clubs
and sailboats.

These composite materials are expensive,
and so their use is confined to relatively high cost
items. On the other hand, even though the raw
materials for these advanced composites are expen-
sive, over 70% of the costs associated with such
composites result from the processing costs for their
manufacture.

In particular, the currently used manu-
facturing processes produce volatiles during curing
of the polymer matrix and such volatiles produce
voids in the matrix which act as sites for structural
failure. In order to minimize void formation during
evolution of volatiles, the cure must be carried out

over a long period, under reduced pressure and this manufacturing requirement is a major factor in the production cost.

Acetylenic groups have been proposed in polymers in order to provide reactive sites for cross-linking the polymers when heated. The potential advantage of such acetylenic groups is that no volatiles will be produced during curing or cross-linking.

The acetylenic groups have been introduced into polymer chains as terminal groups, pendant groups or internal groups.

Acetylene precursor polymers have been reviewed by Hergenrother (P. M. Hergenrother, J. Marcromol. Sci.-Rev. Macromol. Chem. C19(1), 1-34 (1980).

Most of the polymers with terminal acetylenic groups, that have been synthesized contain unsubstituted ethynyl groups on the ends of the polymer chains and they are generally end-capped low molecular weight oligomers which are synthesized in order to provide easier processability. Reinhardt et al (B. A. Reinhardt, F. E. Arnold and M. R. Unroe, U.S. Patent 4,513,131 (1985)) have synthesized the simple bis(phenylethynylphenyl)ethers as potentially thermally curable resins and studied their thermal curing properties.

Polymers containing pendant phenylethynyl groups have been synthesized and these polymers have been thermally cured. Examples are described in the afore-mentioned Hergenrother article and in U.S. Patent 4,375,536 (1983) of Hergenrother.

Polymers containing internal acetylene groups have been less studied. T. Takeichi, H. Date and Y. Takayama, J. Pol. Sci. Chem. Ed. 28, 1989 (1990) describes the synthesis of polyimides contain-

-3-

ing internal acetylene groups. The authors indicate
that the diphenylacetylene groups must be linked in
the metal position to provide effective cross-
linking.

5   **Synthesis of Diarylacetylenes**

Synthetic methods are reviewed in "Compre-
hensive Organic Chemistry" Pergamonn Press, 1979,
Vol. 1 and in The Chemistry of the Carbon-Carbon
Triple Bond, Ed. Saul Patai, John Wiley & Sons 1978,
10   Part 2.

I. Dehydrohalogenation Reactions

The most common method of synthesis is by
dehydrohalogenation reactions of iodo, bromo or
chloro compounds with strong bases, usually KOH,
15   NaOH, alkoxides such as sodium methoxide or potassium
tertiary butoxide or sodamide, or with hydrides, e.g.
sodium hydride or with organometallic compounds such
as butyl lithium.

$$\left.\begin{array}{l} \text{-CHX-CHX-} \\[4pt] \text{-CH}_2\text{-CX}_2\text{-} \\[4pt] \text{-CH=CX-} \\[4pt] \text{>C=CHX---} \end{array}\right\} \xrightarrow{\text{base}} \quad \text{---C}\equiv\text{C---} \qquad X = I, Br, Cl$$
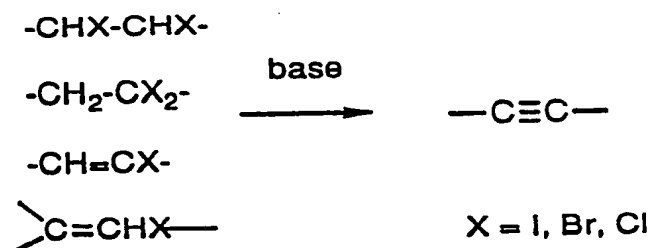
20   The elimination of other groups, thiols,
sulfides, sulfonic acids, phosphate esters, trialkyl
tin hydrides and the elimination of tertiary amines
in a Hofmann elimination has also been observed (pp.
776-81 of the afore-mentioned S. Patai).

-4-

II. Displacement Reactions

Copper acetylides can react with aryl halides to give diarylacetylenes (p 796 of S. Patai) and aryl halides also react with acetylenes in the presence of palladium catalysts (p 798 of S. Patai):

$$Ar-X \;+\; Ar'-C\equiv C-Cu \;\longrightarrow\; Ar'-C\equiv C-Ar$$

$$Ar-X \;+\; Ar'-C\equiv C-H \;\xrightarrow{\text{Pd cat.}}\; Ar'-C\equiv C-Ar$$
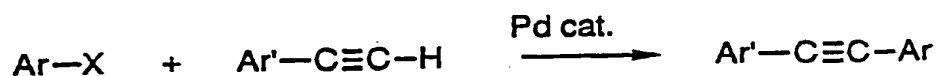
Benzotriazole, benzimidazole and triazoles have been shown by Katritzky to behave as pseudo-halogens in certain reactions, (e.g. A. R. Katritzky, Q.-H. Long and P. Lue, Tetrahedron Letters, 32,3597 (1991) they have demonstrated that dienamines can be synthesized from substituted benzotriazoles by reaction with sodium hydride.
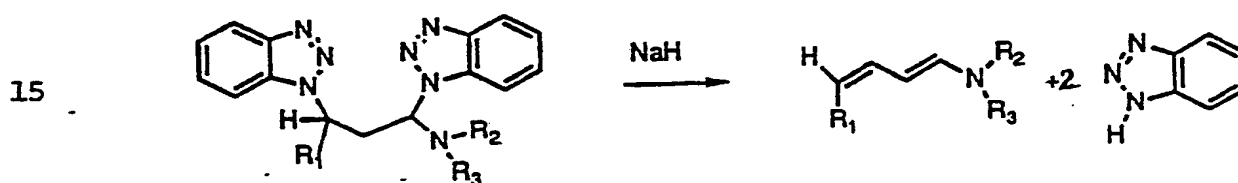
In this reaction the benzotriazole moiety behaves as a pseudohalogen and is eliminated with base in the same way a halogen like bromine would be.

-5-

This is discussed further in a review article (A.R. Katritzky, S. Rachwal and G. J. Hutchings, Tetrahedron 47,2683 (1991).

5   The production of enamines is described in U.S. Patent 5,011,998 (1991) of A. S. Hay et al. As described by Hay et al, the enamines are readily hydrolyzed to deoxybenzoins which in turn are readily oxidized to benzils which are useful in the production of a variety of polymers.

10   Published European Patent Applicaton 0,076,628, Rohm and Haas Company describes certain enamines having fungicidal activity.

DISCLOSURE OF THE INVENTION

This invention provides a novel synthesis
15   for chemical intermediates for polymer production.

This invention also provides processes for the production of diarylacetylenes.

Further, this invention provides a process for the production of enamines.

20   Still further this invention provides novel enamines.

This invention also provides a novel process for producing polymers having acetylenic linkages.

25   Still further this invention provides novel polymers incorporating acetylenic linkages.

In accordance with one aspect of the invention there is provided a process for producing a chemical intermediate for polymer manufacture com-
30   prising: reacting a Schiff's base of formula (III):

$$Ar_1CH=NAr_2 \qquad\qquad (III)$$

-6-

with an N-arylmethylheterocycle of formula (IV):

$$Ar_3-CH_2-N\Big)$$ (IV)

in a basic medium wherein Ar_1, Ar_2 and Ar_3 are each
independently selected from aryl and hetaryl, unsub-
5   stituted or substituted, one or more times, by
radicals selected from F, Cl, Br; alkyl of 1 to 6
carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of
6 to 12 carbon atoms; aralkyl of 7 to 18 carbon
atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1
10   to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms;
aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6
to 12 carbon atoms; and $-N\Big)$ is a hetaryl radical.
        If the process is operated under conditions
favouring the elimination of the heterocyclic of
15   formula (V):

$$H-N\Big)$$ (V)

the reaction proceeds to form a diarylacetylene of
formula (I):

$$Ar_1-C\equiv C-Ar_3$$ (I)

20   in which Ar_1 and Ar_3 are as defined above, as the
favoured reaction.
        If the process is operated under conditions
which do not favour elimination of the heterocyclic
of formula (V):

25      $$H-N\Big)$$ (V)

-7-

the reaction forms an enamine of formula (II):

$$Ar_1-CH=C-Ar_3 \qquad (II)$$
$$\underset{\underbrace{N}}{\overset{|}{}}$$

wherein Ar_1, Ar_3 and $-N\,)$ are all as defined above.

In another aspect of the invention there is provided enamines of formula (II), as defined above, in which the hetaryl radical $-N)$ is other than imidazolyl.

In yet another aspect of the invention there is provided a process for producing diaryl-acetylenes from the enamines (II).

In still another aspect of the invention there is provided a process of producing polymers and copolymers incorporating acetylenic compounds.

In yet another aspect of the invention there is provided novel polymers and copolymers having acetylenic groups incorporated therein.

DESCRIPTION OF PREFERRED EMBODIMENTS

i)   Synthesis of Intermediates

A novel synthesis of the invention com-prises the reaction of the Schiff's base of formula (III), as defined above with the N-arylmethylhetero-cycle of formula (IV), as defined above in a basic medium.

This reaction can produce a diarylacetylene of formula (I), as defined above, or an enamine of formula (II), as defined above, or a mixture contain-ing both.

The hetaryl radical $-N$) is, in particular, one which behaves as a pseudohalogen, and if the reaction conditions favour elimination of the hetero-cycle of formula (V):

-8-

$$H - N \Big)$$ (V)
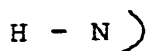
the reaction proceeds with formation of the diaryl-acetylene (I) as the major reaction product, whereas if the reaction conditions do not favour elimination of heterocycle (V), the reaction proceeds with formation of the enamine (II) as the major reaction product.

In general, higher reaction temperatures in conjunction with strongly basic conditions favour the elimination reaction which results in the diaryl-acetylene (I) as the major reaction product. In contrast, lower reaction temperatures in conjunction with weakly basic conditions do not favour the elimination reaction, thus leading to the enamine (II) as the major reaction product.

Reaction time is also a factor in determin-ing whether the diarylacetylene (I) or the enamine (II) is the dominant reaction product.

Depending on the inter-relationship between these different process parameters, the reaction product may be predominantly the diarylacetylene (I) or the enamine (II), or a mixture of both in varying proportions.

The reaction resulting in the diarylacety-lene (I) proceeds via the enamine (II) as an inter-mediate. The diarylacetylene (I) can be produced from the intermediate enamine (II) in situ, or the enamine (II) can be recovered or isolated from the reaction medium and subjected to conditions favouring formation of the diarylacetylene (I).

Thus the invention contemplates reaction of the Schiff's base (III) and the N-arylmethylhetero-cycle (IV) under basic conditions favouring elimi-nation of the heterocycle (V) so that the reaction proceeds to the diarylacetylene (I) via the enamine

-9-

(II).   The invention also contemplates reaction of
(III) and (IV) under first basic conditions which do
not favour elimination of the heterocycle (V) to
produce the enamine (II), and thereafter, possibly
with prior isolation of the enamine (II), reacting
the enamine (II) under second basic conditions
effective for elimination of the heterocycle (V) to
produce the diarylacetylene (I).

The invention also contemplates the elimi-
nation process in which the diarylacetylene (I) is
produced from the enamine (II), as starting material.

ii)   Process Parameters for Synthesis

The synthesis i) is carried out under basic
conditions, more especially in a basic medium.

In particular, the medium suitably com-
prises a polar, aprotic organic solvent, for example,
dimethylformamide, dimethylacetamide or N-methylpyr-
rolidone, which medium is rendered basic. The base
character.may be achieved by the presence of a base,
for example, sodium or potassium tert-butoxide,
sodium amide or sodium dimethyl amide; the sodium
dimethyl amide may be generated <u>in situ</u> from sodium
in N,N-dimethyl formamide. Mixtures of the bases may
be employed.

As indicated above the base selected plays
a role in determining whether the formation of the
diarylacetylene (I) or the enamine (II) is favoured.

Since some heterocycles (V) have a strongly
acidic character, the heterocycle (V) formed as a
by-product of the formation of the diarylacetylene
(I) from the enamine (II), may act as a buffer in the
reaction medium, weakening the basic character and
favouring termination of the reaction with formation
of enamine (II).

-10-

The synthesis can be carried out conveniently at temperatures in the range of 0 to 100°C.; while still lower or higher temperatures. outside this range can be employed; there is no advantage in employing temperatures outside this range.

In general lower temperatures in the range favour the first stage of the reaction to produce enamine (II) as the major reaction product. On the other hand, higher temperatures alone do not dictate continuation of the reaction through the enamine (II) to the diarylacetylene (I); and at the higher temperatures, the reaction time and the strength of the basic character of the reaction medium play a significanat role in determining which reaction product, (I) or (II), dominates; and, as indicated above, when considering the basic character of the reaction medium, it is not only the strength of the base employed which is to be considered, because the acidity of by-product heterocycle (V) also affects the basic character.

On the other hand, a surprisingly fast reaction to form a high yield of diarylacetylene (I) has been observed employing a basic reaction medium of potassium t-butoxide in dimethylformamide even when benzotriazole, which is strongly acidic, was formed as the by-product heterocycle (V). At a temperature of 75°C. the reaction proceeded to form the diarylacetylene in high yield in a reaction time of less than 1 minute.

At lower temperatures, however, the benzotriazole released buffered the reaction to favour the enamine (II) as the reaction product.

-11-

The rapid reaction with benzotriazole as
the heterocyclic (V) presumably results from the high
electron withdrawing character of the benzotriazolyl
radical.

5   iii)   Reactants

The Schiff's bases (III) are readily
produced in condensation reactions between aromatic
aldehydes and aromatic amines, a reaction fully
described in prior literature.

10   The N-arylmethylheterocycles (IV) are
readily produced by the reaction between arylmethyl-
halides and aromatic heterocyclic compounds under
conditions for elimination of hydrogen halide, a
reaction fully described in prior literature.

15   The aryl radicals Ar_1, Ar_2 and Ar_3 are
suitably aromatic radicals having 6 to 16 carbon
atoms in the aromatic nucleus, independently selected
from:

(R)x

(R)x

(R')y
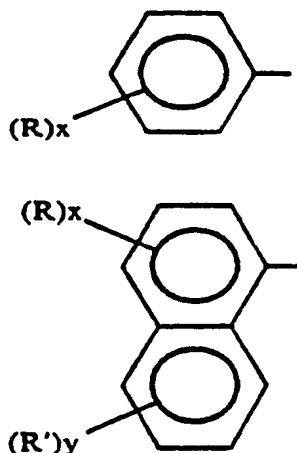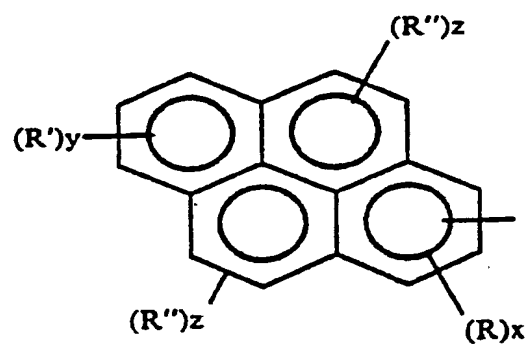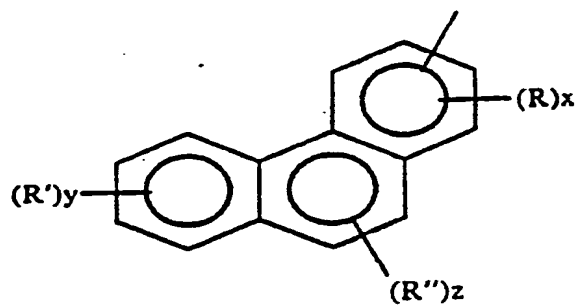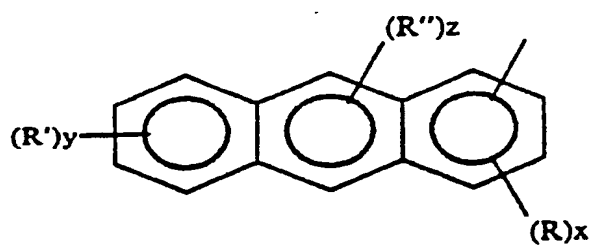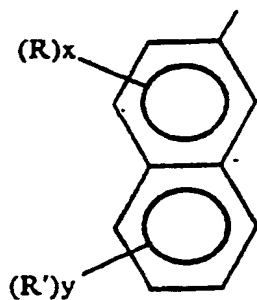
-13-

wherein x and y are integers independently selected from 0, 1, 2 or 3, z is an integer independently selected from 0, 1 or 2 and R, R' and R" are each independently selected from halogen atoms selected

5   from fluorine, chlorine and bromine; alkyl of 1 to 6 carbon atoms, alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms, aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms; alkoxy of 1 to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms;

10   aryloxy of 6 to 12 carbon atoms and thioaryloxy of 6 to 12 carbon atoms.

The hetaryl radicals Ar_1, Ar_2 and Ar_3 may be, for example, pyridinyl, furanyl, thiophenyl, thiazolyl or quinolinyl, which may be unsubstituted

15   or substituted in the manner of the aryl radicals described above; for example the radicals:
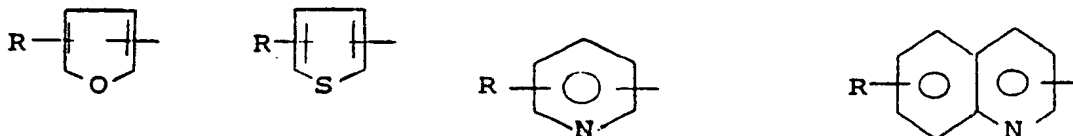
The heterocyclic radical:

20   may be, for example, a benzimidazolyl, benzotriazolyl, triazolyl or tetrazolyl, which radicals may be unsubstituted or substituted. It will be understood that the nature of the substituent is immaterial, provided that it does not interfere with the

25   reaction to produce the desired enamine (II) or diarylacetylene (I).

-14-

iv)   Polymer Production
              Diarylacetylenes of formula (VI):

$$X_1-Ar_4-C\equiv C-Ar_5-X_2 \qquad\qquad (VI)$$

in which X_1 and X_2 are independently selected from F
and OH, and Ar_4 and Ar_5 are aryl or hetaryl as
defined for Ar_1 and Ar_3, are starting materials for
producing polymers which incorporate acetylenic
groups.

              The diarylacetylenes (VI) in which X_1 and
X_2 are both fluorine are within formula (I) and are
produced by the previously described synthesis of the
invention.

              The diarylacetylenes (VI) in which at least
one of X_1 and X_2 is a hydroxyl are produced from the
corresponding diarylacetylenes (VI) in which X_1 and
X_2 are fluorine, by hydrolysis of one or both
fluorine substituents or etherification of one or
both fluorine substituents and hydrolysis of the
resulting alkoxy or aryloxy substituents.

              The reaction to replace one or both
fluorine substituents by an alkoxy or aryloxy is a
novel reaction and it was surprising that such
reaction would proceed efficiently. It appears that
the acetylenic linkage activates the fluorine atom,
facilitating its displacement, but this was not to
have been expected.   The reaction proceeds
efficiently in the presence of an alkali metal
alkoxide or aryloxide in a polar, aprotic organic
solvent.   The reaction is illustrated in the follow-
ing scheme

-15-

$$F-Ar_4-C{\equiv}C-Ar_5-X \; + \; 2-OR \qquad F-Ar_4-C{\equiv}C-Ar_5-OR$$

$$RO-Ar_4-C{\equiv}C-Ar_5-OR$$
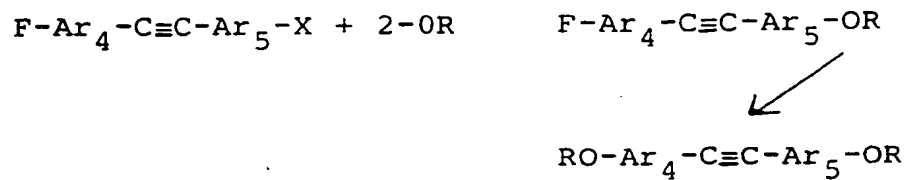
in which X is H or F and R is alkyl or aryl, and Ar_4 and Ar_5 are as defined previously.

5   The production of homopolymers and copolymers, particularly poly(arylether)s, polyesters, polycarbonates and polyformals from diarylacetylenes (VI) is illustrated below:
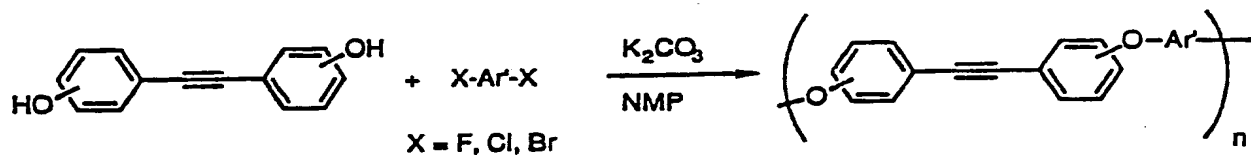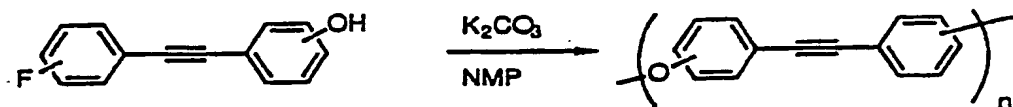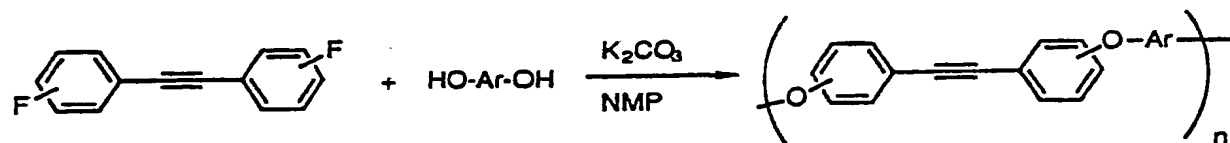
POLY(ARYL ETHER)S

POLYESTERS
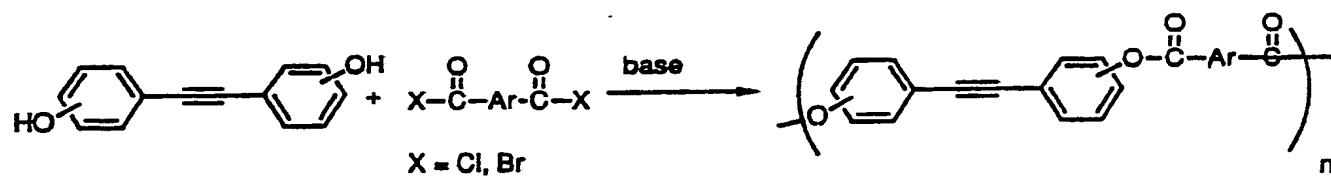
POLYCARBONATES and POLYFORMALS
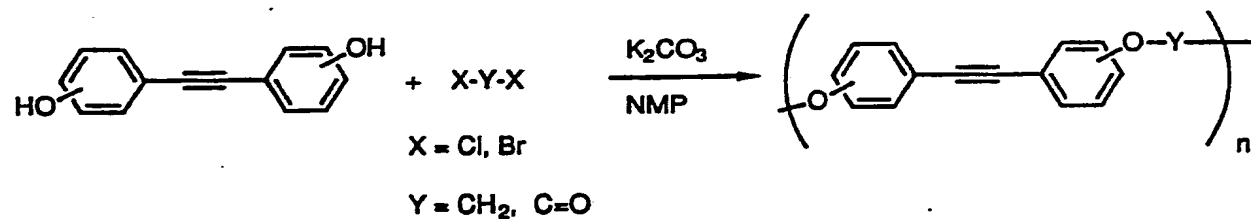
-17-

In these reactions n is an integer indicating the length of the polymer chain.

Any bisphenol can be employed as the reactant HO-Ar-OH in the production of the poly(aryl-ether). The radical Ar_1 is an aromatic moiety such as diphenylsulfone or benzophenone. When X is fluorine Ar_1 can also be a heterocyclic which activates the fluorine for nucleophilic substitution, for example, pyridine, benzoxazole, quinoxaline, an isoquinoline or a phthalazine.

Thus in another aspect of the invention there is provided a process for producing an acetylenic group-containing polymer or copolymer of the formula (VII):

$$Z_1 \!-\!\!\left(Ar_4\!-\!C\!\equiv\!C\!-\!Ar_5\!-\!Y_1\!-\!Z_3\!-\!Y_2\right)_{\!n-x}\!\!-\!(X)_x^{-}\;\;Z_2 \qquad (VII)$$

wherein Z_1 is fluorine, hydroxyl or mercaptyl, Z_2 is hydrogen or fluorine, Z_3 is $-O-$, $-S-$, $-CH_2-$, $-CO-$, $-CO-Ar_6-CO-$ or $-Ar_7-$, in which Ar_6 and Ar_7 are selected from divalent aromatic linkages, Y_1 and Y_2 are each selected from $-O-$ and $-S-$, provided that when Z_3 is $-O-$ or $-S-$, Y_1 and Y_2 are both single bonds, Ar_4 and Ar_5 are each independently selected from arylene and hetarylene, unsubstituted or substituted one or more times by radicals selected from F, Cl, Br, alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms, thioalkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 12 carbon atoms and thioaryloxy of 6 to 12 carbon atoms; X is $-Ar_4-C\equiv C-Ar_5$ or a copolymer unit, n is an integer of 2 to 200, x is an integer of 0 to 199 and n is >x.

-18-

It will be understood that the two basic units of (VII) may be in a random or non-random arrangement or sequence in the case of a copolymer.

In still another aspect of the invention there is provided an acetylenic group-containing polymer or copolymer of formula (VII) as defined above provided that when the polymer or copolymer has acetylenic units $-Ar_4-C=C-Ar_5-$ at both terminal positions, n is at least 3.

The divalent linkages $-Ar_7-$ are in particular derived from dihydroxy aromatics, for example, bisphenols, or from dihaloaromatics in which the halo groups are activated by the presence of electron withdrawing groups such as sulphonyl or carbonyl groups.

Aromatic groups having electron withdrawing groups are thus, for example:

-Ar-CO-Ar- and

$-Ar-SO_2-Ar-$
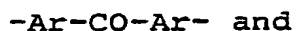
in which the Ar groups are the same or different and are arylene or hetarylene.

The divalent aromatic linkages Ar_6 are selected from a broader class than Ar_7 since no electron withdrawing group is required in Ar_7.

The copolymer unit X may be derived from a wide variety of comonomers, for example, the following comonomer units in which the free valencies are in ortho or para positions.

-19-
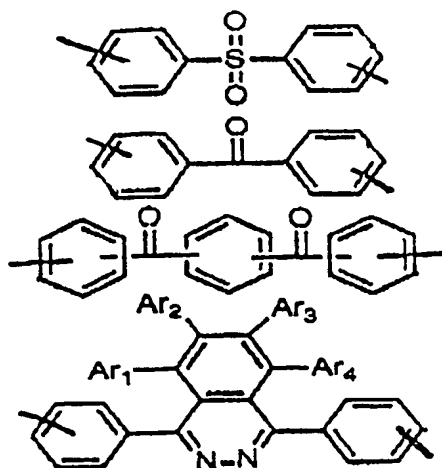
in which Ar$_1$, Ar$_2$, Ar$_3$ and Ar$_4$ are independently selected from unsubstituted and substituted aryl.
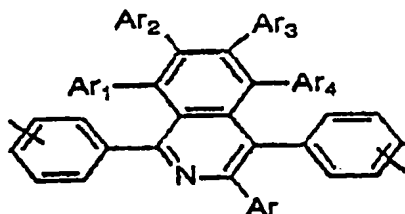
5   in which Ar$_1$, Ar$_2$, Ar$_3$ and R$_4$ are as defined above and Ar is aryl.
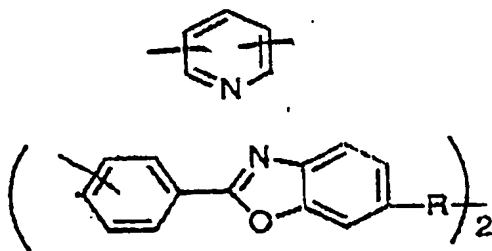
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in which R$_2$ is alkylene or arylene
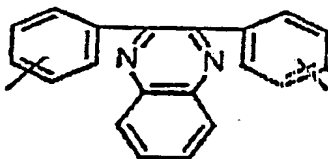
The aromatic moieties of the dihydroxy aromatics may be, for example, arylene and biarylene moieties including the following:
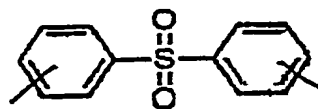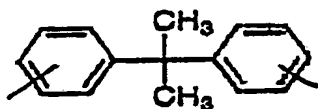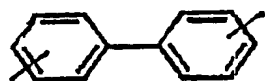
The diarylacetylenes (I) as a class can be readily oxidized to corresponding benzils useful in synthesis of a variety of polymers including poly-quinoxalines, polyphenyls and phthalic anhydrides and

5   the latter can be reacted with diamines to produce polyimides.

The enamines (II) of the invention are useful for the production of deoxybenzoins which can be oxidized to benzils which have utility in the

10   production of polymers. The processes, involving use of enamines, described in U.S. Patent 5,011,998, the teachings of which are hereby incorporated herein by reference, apply to the enamines (II) of the present invention.

15   Thus deoxybenzoins, benzils and polymers may be produced using the enamines (II) of this invention, and the procedures described in U.S. Patent 5,011,998, incorporated herein by reference.

EXPERIMENTAL

$$\text{Ar CH}_2\text{Cl} + \text{Ar}_2\text{H} \xrightarrow[\text{CH}_3\text{CN}]{\text{K}_2\text{CO}_3} \text{Ar CH}_2\text{Ar}_2$$

Ar = Aryl group

Ar₂H =
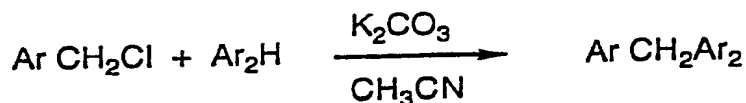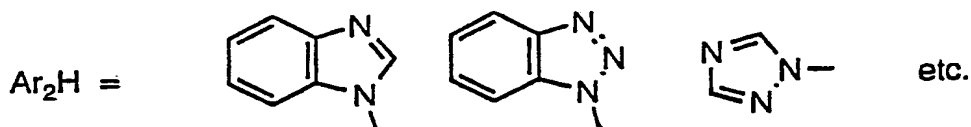
I. Synthesis of N-Benzyl-substituted Heterocyclics

Example 1.

(Phenylmethyl)-1*H*- benzimidazole. To benzyl chloride (13 g, 0.103 mol), 1*H*-benzimidazole (11.81 g, 0.10 mol), K_2CO_3 (60 g, 0.434 mol) was added acetonitrile (200 mL) and the mixture was stirred and heated under reflux for 3 h, filtered hot, and washed with hot CH_3CN (100 mL). The solvent of the filtrate was evaporated and the residual mass recrystallized as needles (16.5 g, 79%): mp 119-120°C (benzene) (lit[1] mp 105°C); ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.40 (s, 2H, C$\underline{H}_2$), 7.20-7.41 (m, 8H), 7.85-7.89 (m, 1H), 8.02 (s, 1H, NC$\underline{H}$N); IR ($CDCl_3$) 3093 (w), 3065 (w), 3037 (w), 2929 (w), 1615 (w), 1496 (s), 1456, 1385 (w), 1361, 1331, 1285, 1261, 1204, 1181, 1007 (w), 963 (w), 947 (w) cm⁻¹. MS (EI) *m/e* 208 (M⁺, 57.8), 91 (100); Anal. Calcd for $C_{14}H_{22}N_2$ (208.26): C, 80.74; H, 5.81; N, 13.45; Found: C, 80.70; H, 6.02; N, 13.31.

[1]Feigl, F.; Gleich, H. *Monatsh.* **1928**, *49*, 385-400.

Example 2.

(Phenylmethyl)-1*H*- benzotriazole. (Phenylmethyl)-1*H*-benzotriazole was prepared from 1*H*-benzotriazole (11.91 g, 0.100 mol) and benzyl chloride as in Example 1 for 1 hour to give the title compound and (phenylmethyl)-2*H*- benzotriazole in a ratio of 75:25.Workup and two recrystallizations gives the pure 1*H*-isomer: mp 117-119 °C (CH_3CN); (lit.[1] mp 114-117 °C; lit.[2,3] mp 115-116 °C)

[1]Claramunt, R. M.; Elguero, J.; Garceran, R. *Heterocycles* **1985**, *23*, 2895.

[2]Märky, M; Schmid, H; Hansen, H. J. *Helv. Chim. Acta* **1979**, *62*, 2129.

[3]Rondeau, R. E.; Rosenberg, H. M.; Dunbar, D. J. *J. Mol. Spectry.* **1969**, *29*, 305.

Example 3.

−23−

(Phenylmethyl)-1*H***- [1,2,4-triazole].**   (Phenylmethyl)-1*H*-[1,2,4-triazole] was prepared from 1*H*-[1,2,4-triazole] (69.7 g, 0.100 mol) and benzyl chloride as in Example 1 for 1 hour to give the title compound and (phenylmethyl)-2*H*-[1,2,4-triazole]. Workup and recrystallization gave the pure 1*H*-isomer (54%): mp 52-53°C (cyclohexane); (lit.[1] mp 54 °C).

[1]Claramunt, R. M.; Elguero, J.; Garceran, R. *Heterocycles* **1985**, *23*, 2895.

Example 4.

(2-Naphthalenyl)methyl-1*H***-benzotriazole.** A procedure similar to Example 2 from 1*H*-benzotriazole and 2-naphthylmethyl chloride gave the title compound after recrystallization in 45% yield: mp 152-153 °C (CH$_3$CN); ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.03 (s, 2H, CH$_2$), 7.32-7.38 (m, 4H), 7.48-7.53 (m, 2H), 7.77-7.83 (m, 4H), 8.07-8.12 (m, 1H).

Example 5.

(1-Naphthalenyl)methyl-1*H***-benzotriazole.** A procedure similar to Example 2 from 1*H*-benzotriazole and 1-naphthylmethyl chloride gave the title compound after recrystallization in 85% yield: mp 149-151 °C (EtOAc/petroleum ether 35-60 °C abbreviated elsewhere as PE); ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.36 (s, 2H, CH$_2$), 7.29-7.59 (m, 7H), 7.87-7.93 (m, 2H), 8.06-8.11 (m, 1H), 8.21-8.26 (m, 1H).

Example 6.

(4-Fluorophenyl)methyl-1*H***-benzotriazole.** In a procedure as in Example 2 but using 1*H*-benzotriazole (23.8 g, 0.200 mol), 1-(chloromethyl)-4-fluorobenzene (29.0 g, 0.200 mol) and K$_2$CO$_3$ (70 g) in CH$_3$CN (300 mL) for 1 hour gave the title compound and (4-fluorophenyl)methyl-2*H*-benzotriazole. Workup and recrystallization gave the mixture of the 1*H* and 2*H*-isomers (75 % yield) which was used in the subsequent reactions. A sample (5 g) was chromatographed (PE/EtOAc 9:1) eluting first the 2*H* isomer and then the title compound: mp 92-94 °C (cyclohexane); ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.82 (s, 2H, CH$_2$), 7.00-7.06 (m, 2H), 7.25-7.46 (m, 5H), 8.08 (d, J=8.9 Hz, 1H); IR (CDCl$_3$) 3052 (w), 2938 (w), 1609, 1513, 1451 (w), 1351 (w), 1315 (w), 1269 (w), 1230 (s), 1159, 1084 cm^{-1}. MS (EI) *m/e* 227 (M$^+$, 52.6), 198 (100), 109 (96.9); Anal. Calcd for C$_{13}$H$_{10}$N$_3$F (227.24): C, 68.71; H, 4.44; F, 8.36; N, 18.49; Found: C, 68.44; H, 4.44; F, 8.40; N, 18.57.

Example 7.

(3-Fluorophenyl)methyl-1*H***-benzotriazole.** In a procedure as in Example 2 but using 1*H*-benzotriazole (20.6 g, 0.173 mol), 1-(chloromethyl)-3-fluorobenzene

-24-

(25.0 g, 0.173 mol), K_2CO_3 (35.9 g) and CH_3CN (150 mL) for 1h gave the title compound and (3-fluorophenyl)methyl-2H-benzotriazole. Similar workup and recrystallization gave the pure 1H-isomer (73%): mp 103-104°C (cyclohexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.87 (s, 2H, CH_2), 6.97-7.08 (m, 3H), 7.29-7.49 (m, 4H), 8.10 (d, J=8.0 Hz, 1H); Anal. Calcd for $C_{13}H_{10}N_3F$ (227.24): C, 68.71; H, 4.44; Found: C, 68.40; H, 4.67.

Example 8.

(2-Fluorophenyl)methyl-1H-benzotriazole. In a procedure as in Example 2 but using 1H-benzotriazole (34.5 g, 0.289 mol) and 1-(chloromethyl)-2-fluorobenzene (41.8 g, 0.289 mol) for 1h gave the title compound and (2-fluorophenyl)methyl-2H-benzotriazole in a ratio of 80:20. Similar workup and recrystallization gave the pure 1H-isomer (73%): mp 93-95°C (cyclohexane); ^{1}H NMR (270 MHz, $CDCl_3$) δ 5.93 (s, 2H, CH_2), 7.08-7.47 (m, 7H), 8.10 (d, J=7.2 Hz, 1H).

II. Synthesis of Schiff Bases

$$Ar_3CHO + Ar_4NH_2 \longrightarrow Ar_3CH=NAr_4 + H_2O$$
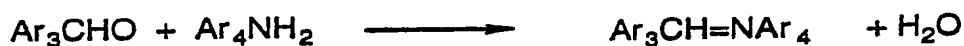
$$Ar_3, \ Ar_4 = \text{Aryl group}$$

Example 9.

N-[(4-fluorophenyl)methylene]benzenamine. To 4-fluorobenzaldehyde (24.8 g, 0.200 mol) and aniline (18.6 g, 0.200 mol) was added benzene (200 mL) and acetic acid (0.7 mL) and the mixture is heated under reflux until all the water (3.6 mL) was azeotropically removed. The solvent is evaporated and the residual oil upon cooling and stirring crystallized. The white mass was then recrystallized as needles (28 g, 70%) : mp 39-40 °C (PE) (lit.[1] mp 40 °C).

[1]Dayal, S. K.; Ehrenson, S.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 9113.

Example 10.

N-[(3-fluorophenyl)methylene]benzenamine.[1,2] A similar procedure as for the preparation of N-[(4-fluorophenyl)methylene]benzenamine (no acetic acid required) gave an oil which was distilled (87%): bp 100-101°C/0.75 mm Hg.

[1]Liepins, E.; Pestunovich, V. A.; Eremeev, A. V.; Tikhomirov, D. A.; Gaidarova, N. P. *Kim. Geterotsikl. Soedin.* **1977**, 906-909; *Chem. Abstr.* **1977**, *87*, 183795b.
[2]Fauran, C.; Bergeron, H.; Raynaud, G.; Thomas, J.; Eberle, J. Fr. Demande 2, 262, 513 26 Sep 1975; *Chem. Abstr.* **1976**, *84*, 121843v.

-25-

Example 11.

N-[(2-fluorophenyl)methylene]benzenamine. A similar procedure as for the preparation of N-[(4-fluorophenyl)methylene]benzenamine (no acetic acid required) gave an oil which was distilled (90%): bp 103-104°C/1.5 mm Hg pressure; (lit.[1] bp 135°C).

[1]Kessar, S. V.; Gopal, R.; Singh, M. *Tetrahedron* **1973**, *29*, 167.

III. Synthesis of Enamines

$$\text{Ar CH}_2\text{Ar}_2 \quad + \quad \text{Ar}_3\text{CH=NAr}_4 \quad \longrightarrow \quad \text{Ar}_3\text{—CH=C—Ar}$$
$$\overset{|}{\text{Ar}_2}$$
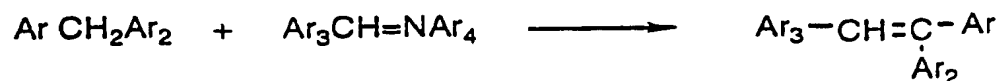
(1,2-diphenylethenyl)-1*H*-benzotriazole.

Example 12. Method 1.

To a mixture of powdered KOH (2.24 g, 0.040 mol) and DMF (18 mL) there was added with rapid stirring phenylmethyl-1H-benzotriazole (1.05 g, 0.005 mol) and N-phenylmethylenebenzenamine (0.905 g, 0.005 mol) in DMF (7 mL) at 75 °C. After five minutes the reaction was poured into ice-cold water (75 mL) and left to crystallize the title enamine. This was filtered, washed with water, and dried to yield 1.07 g (72%) of the title enamine. An analytical sample was chromatographed PE/EtOAc 4:1 and recrystallized with charcoal treatment: mp 152-154 °C (cyclohexane); Anal. Calcd for $C_{20}H_{15}N_3$ (297.36): C, 80.78; H, 5.08; N, 14.13; Found: C, 80.66; H, 5.14; N, 14.14.

Example 13. Method 2.

A procedure similar to Example 12 except that instead of KOH potassium t-butoxide (0.56 g, 0.005 mol) was used. At 75 °C the reaction was complete and worked up as above. Chromatography first with PE elutes some (5-10%) diphenyl acetylene and then PE/EtOAc 4:1 elutes the title enamine (75-80%). This method was applied to other bases as given in Table 1.

Example 14.

(1,2-Diphenylethenyl)-1*H*-benzimidazole. A procedure as in Example 13 using (phenylmethyl)-1H- benzimidazole gave the enamine (82%): mp 141-143 °C (cyclohexane); ^{1}H NMR (300 MHz, CDCl3) δ 6.82 (m, 2H), 6.98 (d, J=8.0 Hz, 1H), 7.14-7.19 (m, 5H), 7.25-7.38 (m, 6H), 7.83 (s, 1H, NCHN), 7 (88, J=d, 9.0 Hz,

-26-

1H); IR (CDCl$_3$) 3085 (w), 3063, 3032 (w), 1635, 1611 (w), 1491 (s), 1484, 1452, 1391, 1365 (w), 1308, 1284, 1259, 1218, 1183 (w), 1078 (w), 1031 (w), 1006 (w) cm^{-1}. MS (EI) m/e 296 (M$^+$, 100), 219 (13), 178 (52); Anal. Calcd for C$_{21}$H$_{16}$N$_2$ (296.38): C, 85.11; H, 5.44; N, 9.45; Found: C, 85.03; H, 5.50; N, 9.45.

Example 15.
[1,2-bis(4-fluorophenyl)ethenyl)]-1H-benzotriazole. A procedure as in Example 13 using (4-Fluorophenyl)methyl-1H-benzotriazole. gave the title enamine (60 %): mp 134-136 °C (cyclohexane); MS (EI) m/e 333 (M+, 5), 305 (50), 304 (100), 303 (32), 215 (20), 214 (23), 183 (62); Anal. Calcd for C$_{20}$H$_{13}$F$_2$N$_3$ (333.34): C, 72.06; H, 3.93; F, 11.4; N, 12.61; Found: C, 72.28; H, 3.93; F, 11.11; N, 12.74.

IV. Synthesis of Acetylenes

$$Ar\,CH_2Ar_2 \;+\; Ar_3CH=NAr_4 \longrightarrow Ar_3\!-\!\!\equiv\!\!-\!Ar \longleftarrow Ar_3\!-\!CH\!=\!\underset{\underset{Ar_2}{}}{C}\!-\!Ar$$

Ar, Ar$_3$, Ar$_4$ = Aryl groups
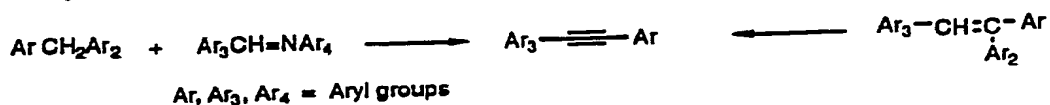
Diphenylacetylene. General Procedure.
Example 16. Method a. To potassium t-butoxide (3.36 g, 30 mmol) in DMF (40 mL) at 75 °C was added as quickly as possible and all at once the [arylmethyl]-1H-benzotriazole (10 mmol) and N-(arylmethylene)benzenamine (10 mmol) dissolved in DMF (10 mL). Within a minute the solution is poured into ice-cold water (150 mL), extracted with CHCl$_3$ (3 x 50 mL) and chromatographed (PE). The acetylenes were recrystallized from MeOH. Thus was obtained: diphenylacetylene (75 %): mp 59-61 °C (MeOH); IR (CDCl$_3$) 1650 (w), 1604 (w), 1589 (w), 1512 (s), 1233, 1155 (w) cm^{-1}.

Example 17. Method b. To potassium t-butoxide (5.6 g, 50 mmol) in DMF (40 mL) at 75 °C was added N-(phenylmethyl)-1H-benzimidazole (2.08 g,10 mmol) and N-(phenylmethylene)benzenamine (1.81 g,10 mmol) dissolved in DMF (10 mL). After 5 hours the solution is poured into ice-cold water (150 mL), extracted with CHCl$_3$ (3 x 50 mL) and chromatographed (PE). Diphenylacetylene was obtained in 73 % yield.

Example 18. Method c.To potassium t-butoxide (5.6 g, 50 mmol) in DMF (40 mL) at 75 °C was added N-(phenylmethyl)-1H-1,2,4-triazole (1.59 g,10 mmol) and N-(phenylmethylene)benzenamine (1.81 g,10 mmol) dissolved in DMF (10 mL). After 30 minutes the solution is poured into ice-cold water (150 mL), extracted with CHCl$_3$ (3 x 50 mL) and chromatographed (PE). Diphenylacetylene

-27-

was obtained in 11 % yield.

Table 1: Influence of different bases and temperatures on the reaction of phenyl-
methy-1H-benzotriazole (5 mmol) and N-phenylmethylenebenzenamine (5 mmol)
in DMF (25 mL) in the production of the enamine (1) and diphenylacetylene (2).

Example	Temp. (°C)	Time (min)	Base (mmol)				Yield (%)	
			NaNH2	Na	t-BuOH	KOt-Bu	1	2
19	75	30	0	22	0	0	0	55
20	75	50	0	4.8	2.3	0	55	5
21	60	30	0	9.1	4.6	0	61	0
22	75	60	0	4.8	0	0	32	0
23	50	20	0	0	0	5	40	35
24	22	20	0	0	0	2.5	60	0
25	0	80	0	0	0	3.57	56	0
26	75	70	15	0	0	0	47	5
27	75	1100	0	22	11	0	3	42

Example 28.

1-(Phenylethynyl)naphthalene. In a procedure similar to that of Example 16 us-
ing [phenylmethyl]-1H-benzotriazole (10 mmol) and N-([1-
naphthalenyl]methylene)benzenamine (10 mmol): 88% yield: mp 51-53°C
(MeOH) (lit[1] oil); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.39-7.69 (m, 8H), 7.77-7.90
(m, 3H), 8.46 (br d, 2.7H, 1H); IR (CDCl$_3$) 3060 (s), 2245 (eyne), 1596, 1581,
1508, 1491 (s), 1442, 1398, 1333, 1215, 1070, 1017 cm^{-1}. MS (EI) m/e 228 (M$^+$,
100).

[1]Dessy, R. E.; Kandil, S. A. *J. Org. Chem.* **1965**, *30*, 3857.

Example 29.

1-Methoxy-4-(phenylethynyl)benzene. Procedure similar to that of Example 16
using [phenylmethyl]-1H-benzotriazole (10 mmol) and N-[(4-
methoxyphenyl)methylene]benzenamine (10 mmol): 67% yield: mp 57-58 °C
(MeOH) (lit.[1] 58-60 °C); ^{1}H NMR (300 MHz, CDCl$_3$) δ 3.84 (s, 3H, OCH$_3$), 6.89

−28−

(d, 1.9H, 2H, C(3 and 5)H), 7.30-7.38 (m, 3H), 7.45-7.54 (m, 4H).

[1] Katritzky, A. R.; Boulton, A. J.; Short, D. J. *J. Chem. Soc.* 1960, 1519.

Example 30.

Bis(4-fluorophenyl)acetylene. To potassium t-butoxide (1.5 g, 13.4 mmol) in DMF (15 mL) at 75 °C was added as quickly as possible and all at once [(4-fluorophenyl)methyl]-1*H*-benzotriazole (1.14 g, 5 mmol) and (4-fluorophenyl)methylenebenzenamine (1.00 g, 5 mmol) dissolved in DMF (10 mL). Within a minute the solution is poured into ice-cold water (75 mL) crystal-lizing the title compound which was filtered and then chromatographed (PE). The acetylene 0.54 g (50%) recrystallizes as needles : mp 95-96 °C (MeOH); (lit.[1] 94-95 °C).

[1] Gascoyne, J. M.; Mitchell, P. J.; Phillips, L. *J. Chem. Soc., Perkin Trans. 2* 1977, 1051.

Example 31.

4-(t-Butoxy)-4'-fluorodiphenylacetylene. A similar procedure as for the prepar-ation of bis(4-fluorophenyl)acetylene in Example 30 but stirred at 75°C for 15 min and then quenched with water gave the title acetylene (15% HPLC) and bis(4-fluorophenyl)acetylene (30% HPLC). Chromatography (PE) elutes the difluoro derivative then PE/EtOAc 97:3 elutes the title compound recrystallizing as color-less plates 2.5 g (10%): mp 102-104°C (MeOH); ^{1}H NMR (200 MHz, CDCl$_3$) δ 1.35 (s, 9H, (CH$_3$)$_3$), 6.93-7.06 (dd, J=8.6 Hz, 4H), 7.39-7.51 (m, 4H); IR (CDCl$_3$) 3020 (w), 2981, 2247 (w,(acetylenic stretch), 1605, 1515 (s), 1474 (w), 1393 (w), 1367, 1281 (w), 1234, 1218, 1157 (s) cm^{-1}. MS (EI) *m/e* 268 (M+ (4.5)), 212 (100), 183-(28), 157 (9.4); Anal. Calcd for C$_{18}$H$_{17}$FO (268.33): C, 80.57; H, 6.39; Found: C, 80.10; H, 6.42.

Example 32.

4,4'Bis(t-Butoxy)diphenylacetylene. A similar procedure as for the preparation of bis(4-fluorophenyl)acetylene.]in Example 30 but using 5 equiv of potassium t-butoxide for 150 minutes and then quenched with water gave the title acetylene (45% HPLC). Chromatography (PE/EtOAc 9:1) and recrystallization with char-coal treatment gave 0.64 g (40%) colorless prisms: mp 129-131°C (MeOH); ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.36 (s, 18H, C(CH$_3$)$_3$), 6.96 (d, J=8.7 Hz, 4H, phenyl C3 and 3'H), 7.43 (d, 4H, phenyl C2 and 2'H); IR (CDCl$_3$) 3040 (w), 2980, 2936 (w), 2907, 2875, 1606, 1511, 1475 (w), 1394, 1367, 1309 (w), 1240, 1158 (s), 1101 (w), 1016 (w) cm^{-1}. MS (EI) *m/e* 322 (M+, 6.1), 266 (4.1), 210 (100).

Example 33.

-29-

1,2-Bis(4-hydroxyphenyl)-ethanone. To a solution of acetic acid (15 mL), c. HCl (2.0 mL) and H_2O (3.0 mL) was added 1,1'-(1,2-ethynediyl)bis[4-(1,1-dimethylethoxy)benzene] (1.0 g, 3.1 mmol) and heated under reflux 1.5 h. Then the solution was poured into ice-cold H_2O (50 mL) precipitating the title compound which was filtered washed with water, air-dried, and recrystallized into tanned needles (.52 g, 80% yield). A second recrystallization with charcoal treatment and acidification of the solution gave colorless needles: mp 217-220°C (H_2O) (lit[1] mp 214-215°C); ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.09 (s, 2H, CH_2), 6.66 (d, J=8.45 Hz, 2H, C9H), 6.82 (d, J=8.7 Hz, 2H, C2H), 7.02 (d, 2H, C8H), 7.89 (d, 2H, C3H), 9.23 (s, 1H, C10OH), 10.34 (s, 1H, C1OH); ^{13}C NMR (300 MHz, DMSO-d_6) δ 43.44 (CH_2), 115.11, 115.20, 125.58, 127.85, 130.36, 130.54, 131.02, 131.17, 155.85, 161.97, 196.18 (C=O); MS (EI) *m/e* 228 (M^+, 4), 121 (100), 107 (14.8), 93 (13), 65 (15).

[1]Zincke, Th.; Fries, K. *Justus Liebigs Ann. Chem.* 1902, *325*, 67.

Example 34.

1-Hydroxy-4-(phenylethynyl)benzene. A procedure similar to that described[1] was used. A sample of 1-methoxy-4-(phenylethynyl)-benzene (0.4 g, 1.9 mmol) was added collidine (3 mL), LiI (1.5 g) and the solution heated under reflux for 5h (>95% conversion). The solution was poured into water acidified with HCl, extracted with ether (3 x 50 mL) and dried (MgSO$_4$). The ether was evaporated and the residue chromatographed (PE) eluting the title compound 0.3 g (80%): mp 125-128°C (cyclohexane) (lit[2] mp 91-92°C, lit[3] mp 83-84°C); ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.80 (d, J=8.77 Hz, 2H, C2H), 7.37 (d, 2H, C3H), 7.35-7.42 (m, 3H), 7.46-7.50 (m, 2H), 9.92 (s, 1H, OH); ^{13}C NMR (300 MHz, DMSO-d_6) δ 87.32 (acetylenic C), 89.98 (acetylenic C), 112.42 (sp^{2}C), 115.74, 122.90 (sp^{2}C), 128.20, 128.66, 131.06, 133.00, 158.06 (COH); IR (CDCl$_3$) 3596 (OH), 3066 (w), 3039 (w), 2217 (w, acetylenic stretch), 1605, 1512, 1429 (w), 1328 (w), 1261 (s), 1219, 1171 (s), 1140 (w), 1099 (w), 834, 805 (w) cm^{-1}. MS (EI) *m/e* 194 (M^+, 100), 165 (29.4), 97 (11.3).

[1]Harrison, I. T. *J. Chem. Soc., Chem. Commun.* 1969, 616.

[2]Veschambre, H.; Dauphin, G.; Kergomard, A. *Bull. Soc. Chim. Fr.* 1967, 2846.

[3]Huysmans, W. G. W. *Dissertation Leiden* 1964.

Example 35.

4,4'-Bis(phenoxy)diphenylacetylene. To 4,4'-difluorotolane (0.5 g, 0.0023 mol) and dry potassium phenolate (prepared from aqueous KOH and phenol with azeotropic removal of H_2O with benzene) (1.5 g, 0.011 mol) was added DMF (10 mL)

-30-

and the mixture heated at 170°C for 12 h after which there appeared a little difluo-
rotolane remaining. This mixture was poured in water, the precipitate was filtered,
washed with water,dried, and the title compound recrystallized as flakes 0.54 g
(64%): mp 171-173°C (acetic acid) (lit.[1] mp 167-168°C); ^{1}H NMR (270 MHz,
CDCl$_3$) δ 6.89 (d, J=8.7 Hz, 4H, phenylene C3,3'H), 6.97 (d, J=8.6 Hz, 4H, phenyl
C2, 2'H), 7.07 (t, J=7.9 Hz, 2H, phenyl C4H), 7.29 (t, 4H, phenyl C3,3'H), 7.40
(d, 4H, phenylene C2,2'H); IR (CDCl$_3$) 3041 (w), 3020 (w), 1590, 1512, 1488,
1312 (w), 1274 (w), 1238 (s), 1218, 1165 (w), 1020 (w) cm^{-1}. When the sample is
placed in a DSC apparatus with a N$_2$ gas flow ramped at 10°C/min it shows a
Tm=163.9°C. In a gas-tight crucible and the temperature ramped at 2°C/min this
sample shows Tm=169.5°C and an exotherm maximum at 359.3°C.The exotherm
begins at ~302°C and ends at ~396°C. Some of this material is heated in a closed
glass capillary tube at 320-330°C for 6 h and then an aliquot of the product was
chromatographed (HPLC). The retention times (tR in min) and area % were: 4.43
(8), 4.63 (6), 9.02 (40), 13.08 (6.5), 19.24 (15).

[1]Lau, K. S.; Arnold, F. E. *Org. Prep. Proced. Int.* **1980**, *12*, 327.

Example 36.

3,3'-Difluorodiphenylacetylene. A similar procedure to Example 30 but using [
(3-fluorophenyl)methyl]-1*H*-benzotriazole and (3-
fluorophenyl)methylenebenzenamine, gave the title acetylene after recrystalliza-
tion (30%) needles: mp 60-62°C (MeOH) (lit.[1] mp 61-62°C, lit.[2] mp 55.5-58°C);
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.04-7.11 (m, 2H), 7.22-7.25 (m, 2H), 7.31-7.35
(m, 4H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 88.89 (2.9, ethynyl C), 115.92 (21.1,
C4), 118.42 (22.9, C2), 124.60 (9.5, C1), 127.54 (2.9, C6), 129.97 (8.7, C5),
162.36 (246.7, C3).

[1]Carpino, L. A.; Chen, H.-W. *J. Am. Chem. Soc.* **1979**, *101*, 390.

[2]Bender, D. F.; Thippesway, T.; Rellahan, W. L. *J. Org. Chem.* **1970**, *35*, 939.

Example 37.

2,2'-Difluorodiphenylacetylene. A similar procedure to Example 30 but using [
(2-fluorophenyl)methyl]-1*H*-benzotriazole and (2-
fluorophenyl)methylenebenzenamine, gave the title acetylene after chromatogra-
phy (PE) and recrystallization (15%) needles: mp 53-54°C (MeOH); ^{1}H NMR
(200 MHz, CDCl$_3$) δ 7.05-7.16 (m, 4H), 7.27-7.38 (m, 2H), 7.50-7.58 (m, 2H);
^{13}C NMR (200 MHz, CDCl$_3$) δ 88.05 (2.6, acetylenic C), 112.03 (15.8, C1),
116.02 (21, C3), 124.49 (3.8, C6), 130.83 (8, C4), 134.06 (C5), 163.24 (253, C2);
IR (CDCl$_3$) 3040 (w), 2228 (w, acetylenic stretch), 1951 (w), 1917 (w), 1883 (w),

-31-

1799 (w), 1700 (w), 1615 (w), 1576, 1501, 1447 (s), 1413 (w), 1321 (w), 1264 (s), 1224 (s), 1155 (w), 1100, 1030 cm⁻¹. MS (EI) *m/e* 214 (M⁺, 100), 107 (12.8).

Example 38.

2,4'-Difluorodiphenylacetylene. A similar procedure to Example 30 but using [(4-fluorophenyl)methyl]-1H-benzotriazole (1.14 g, 5 mmol) and (2-fluorophenyl)methylenebenzenamine (1.00 g, 5 mmol), gave the title acetylene after recrystallization (50%) needles: mp 108-109°C (MeOH); ¹H NMR (200 MHz, CDCl₃) δ 7.0-7.18 (m, 4H), 7.24-7.38 (m, 1H), 7.45-7.59 (m, 3H); ¹³C NMR (200 MHz, CDCl₃) δ 82.77 (acetylenic C1), 93.72 (3.35, acetylenic C1'), 112.21 (15.39, C1), 116.03 (21.07, C3), 116.16 (22.18, C3'), 119.50 (3.41, C1'), 124.50 (3.67, C6), 130.57 (8.04, C4), 133.99 (8.15, C5 or C2'), 134.16 (8.5, C5 or C2'), 163.24 (252.45, C2 or C4'), 163.32 (250.7, C2 or C4'); IR (CDCl₃) 2263 (w), 2247 (etynyl stretch, w), 1600 (C=C), 1574 (w), 1510 (s), 1489, 1451, 1264, 1228, 1156, 1096, 1029 (w) cm⁻¹. MS (EI) *m/e* 214 (M⁺, 100).

Example 39.

3,4'difluorodiphenylacetylene. A similar procedure to Example 30 but using [(4-fluorophenyl)methyl]-1H-benzotriazole (1.14 g, 5 mmol) and (3-fluorophenyl)methylenebenzenamine (1.00 g, 5 mmol), gave the title acetylene after recrystallization (60%) needles: mp 88-89 °C (MeOH).

Example 40.

Bis(2-naphthyl)acetylene. A procedure similar to Example 16 using N-([2-naphthalenyl]methylene)benzenamine and 2-naphthylmethyl chloride gave a 76% yield of product : mp 225-226°C (MeOH) (lit.[1] mp 228-229 °C).

[1]Nakasuji, K.; Akiyama, S.; Akashi, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3567.

Example 41.

Bis(1-naphthyl)acetylene. A procedure similar to Example 16 using N-([1-naphthalenyl]methylene)benzenamine and 1-naphthylmethyl chloride gavea 67% yield of product: mp 127-128°C (MeOH) (lit.[1] mp 129 °C).

[1] Nakasuji, K.; Akiyama, S.; Akashi, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3567.

Example 42.

Methylenebis(4-oxyphenylethynyl)bisbenzene. A procedure similar to Example 16 but using [phenylmethyl]-1H-benzotriazole (2.09 g,10 mmol) and 4,4'-methylenedioxybis(phenylmethylene)dianiline[1] (2.02 g, 5 mmol) for 1 h at 75°C gave after chromatography (PE/EtOAc 4:1) the title acetylene (30%): mp 140-

–32–

143°C (cyclohexane); ^{1}H NMR (200 MHz, CDCl$_3$) δ 5.74 (s, 2H, CH$_2$), 7.05-7.10 (m, 4H), 7.30-7.35 (m, 6H), 7.45-7.52 (m, 8H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 88.58 (acetylenic C), 88.97 (acetylenic C), 90.70, 116.36, 117.41, 123.36, 128.08, 128.31, 131.48, 133.09, 156.72; IR (CDCl$_3$) 3062 (w), 2978 (w), 2911 (w), 2217 (w, acetylenic stretch), 1599, 1573 (w), 1509, 1443 (w), 1414 (w), 1314 (w), 1279 (w), 1233, 1209 (s), 1175, 1137 (w), 1103 (w), 1014, 836 cm^{-1}. MS (EI) *m/e* 400 (M$^+$, 64), 207 (100), 194 (18.7), 177 (83.7), 165 (24.3), 151 (27.0).

[1]Prepared as described previously: Paventi, M.; Hay, A. S. *Synthesis* **1990**, 878.
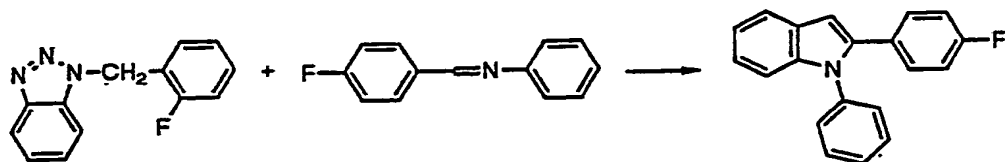
Example 43.

2-(2-Phenylethynyl)furan. A procedure similar to Example 16 but with 2-(N-phenylaminomethylidine)-furan (0.86 g, 0.005 mol) and (phenylmethy)-1H-benzotriazole (1.05 g, 0.005 mol) gave after workup and chromatography (PE/EtOAc 4:1) an oil (90 %, 98.5% pure) (lit.[1] oil bp 74 °C/0.1 mm Hg) which darkened on standing: ^{1}H NMR (270 MHz, CDCl$_3$) δ 6.61 (dd, J$_{34}$3.3, $_{23}$1.98 Hz, 1H, C3H), 6.855 (d, 1H, C4H), 7.52-7.55 (m, 3H, phenyl), 7.616 (d, 1H, C2H), 7.71 (m, 2H, phenyl); [13]C NMR (270 MHz, CDCl$_3$) δ 79.38 (C<u>C</u>(C$_4$H$_4$O)), 93.22 (Ph<u>C</u>C), 111.03 (C4), 115.19 (C3), 122.25 (C1'), 128.35 (C3'), 128.65 (C4'), 131.38 (C2'), 137.12 (C2), 143.59 (C5); MS (EI) *m/e* 168 (M$^+$, 100), 139 (96.8).

[1]Teitei, T.; Collin, P. J.; Sasse, W. H. F. *Aust. J. Chem.* **1972**, *25*, 171.

Example 44.

3-(2-Phenylethynyl)pyridine. A procedure similar to Example 16 but with 3-(N-phenylaminomethylidine)-pyridine (0.911 g, 0.005 mol) and (phenylmethy)-1H-benzotriazole (1.05 g, 0.005 mol) gave after workup and chromatography (PE/EtOAc 4:1) and treatment with boiling PE white needles (80 %): mp 47-48 °C (PE) (lit.[1] mp 47-48.5 °C, acetylenic stretch 2200 cm^{-1}); MS (EI) *m/e* 179 (M$^+$, 100), 126 (21.7).

[1]Castro, C. E.; Gaughan, E. J.; Owsley, D. C. *J. Org. Chem.* **1966**, *31*, 4071.

V. Synthesis of Indoles

-33-

Example 45.

1-Phenyl-2-(4-fluorophenyl)-1*H*-indole. A solution of (2-fluorophenyl)methyl-1*H*-benzotriazole (1.13 g, 5 mmol) and N-[(4-fluorophenyl)methylidine]benzenamine (.996 g, 5 mmol) in DMF (7 mL) was stirred into potassium t-butoxide (1.68 g, 15 mmol) in DMF (18 mL) preheated to 75 °C. The reaction monitore by HPLC showed completion upon mixing. After 11 minutes the DMF solution was poured in ice-cold H_2O (75 mL) extracted with $CHCl_3$ (3 x 50 mL) and the solvent was evaporated. Chromatography first using PE as eluted 1-(4-fluorophenylethynyl)[2-fluorobenzene] (*vide infra*) then the eluant was changed to PE/EtOAc 97:3 eluting the title indole (40 %) : mp 126-128 °C (MeOH); ^{1}H NMR (200 MHz, CDCl$_3$) δ 6.77 (s, 1H, C3H), 6.94 (t, J=8.7 Hz, 2H, phenic H), 7.16-7.48 (m, 10H), 7.66-7.72 (m, 1H); MS (EI) *m/e* 287 (M$^+$, 100).

VI. Polymer Synthesis
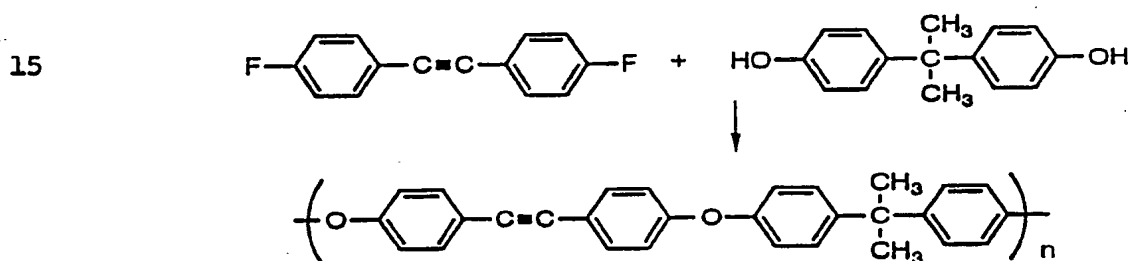
Example 46

Poly(phenylene ether yne) from BPA. A mixture of 4,4'-(1-Methylethylidene)bisphenol (BPA) (1.141 g, 5 mmol), 4,4'-difluorodiphenylacetylene (1.071 g, 5 mmol) and anhydrous K_2CO_3 (0.9 g, mmol) in toluene (10 mL) and N-methylpyrrolidone (NMP) (14 mL) was stirred and heated to the reflux temperature of toluene azeotropically removing the water for 5 hours under a slow stream of N_2. The temperature was allowed to increase to 180 °C over a period of 5 hours allowing for the removal of toluene and NMP (4 mL). The dark mixture was then allowed to stir for an additional 10 hours when an aliquot flooded in MeOH precipitated high molecular weight polymer. The organics were cooled, filtered through celite, precipitated (MeOH),and dissolved in $CHCl_3$, filtered and reprecipitated (MeOH), washed (H_2O) and dried to yield 1.57 g of the title polymer : Tg=163 °C exotherm maximum 398 °C (temperature

-34-

ramped at 20 °C/min), η inh 0.69 dL/g (TCE, 25.4 °C), Mw=54400 Mn=23300. Af-
ter a second scan there was no discernable glass transition temperature indicating
that the polymer is now highly crosslinked. After heating the polymer is also now
completely insoluble in all solvents.

5   **Example 47**
**Poly(phenylene ether yne) from 4,4'–difluorodiphenylacetylene and bis(4-
hydroxyphenyl)-9,9-fluorene**
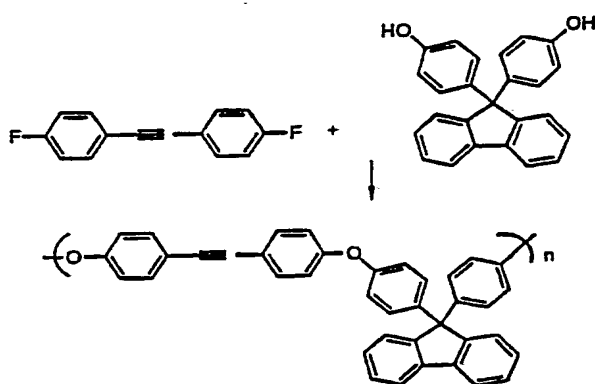
10   4,4'–Difluorodiphenylacetylene (2.1422 g, 0.01000 mol), bis(4-hydroxyphenyl)-
9,9-fluorene (3.50416 g, 0.01000 mol), potassium carbonate (1.52 g, 0.0110 mol)
NMP (28 mL) and toluene (20 mL) were heated at 140 °C for 1h with removal of
water with a Dean-Stark trap under a slow stream of nitrogen. The temperature
was raised to 195°C by bleeding toluene from the system and maintaining this
15   temperature for 4.5h. Heating was discontinued, NMP (15 mL) was added to the
hot polymer mixture. This mixture was then added dropwise to a fast-stirring
MeOH/H2O (600 mL:200 mL) mixture. The resulting precipitated polymer beads
were suction-filtered, washed with water and MeOH and air-dried for 1h. The ma-
terial was dissolved in CHCl3 (200 mL) and filtered through a bed of MgSO4 (.5
20   cm) and celite (4 cm) in a 150 mL fritted funnel and washed with CHCl3 (200
mL). The volume of the filtrate was reduced to 100 mL and the title polymer was
recovered by dropwise addition of this chloroform solution into MeOH (500 mL).
The beads were filtered and air-dried over three days to give a quantitative yield
of the title polymer, Tg=263 °C exotherm maximum 388 °C (temperature ramped
25   at 20 °C/min). After a second scan there was no discernable glass transition tem-
perature indicating that the polymer is now highly crosslinked. After heating the

-35-

polymer is also now completely insoluble in all solvents.

VII. Copolymer Synthesis
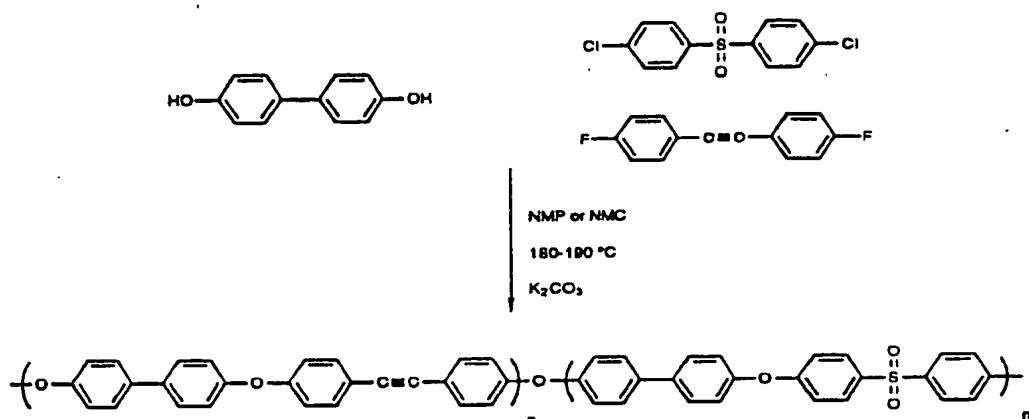
5 The following copolymers were synthesized as in Example 43 using the molar amounts of 4,4'-difluorodiphenylacetylene and 4,4'-dichlorodiphenylsulfone shown in Table 2.

Table 2. Properties of Copolymers

Example	n m mol%	Inherent Viscosity	Tg °C	Tg after curing 1 hr @ 340 °C	TGA °C N2 (-10%) Air		Film	Solubility
48	5 95	0.39	208	218	511	522	brittle	CH2Cl2/CHCl3
49	10 90	0.4	210	225	526	530	brittle	CH2Cl2/CHCl3
50	30 70	0.64	188	277	522	531	brittle	NMP/TCE (hot)

-36-

CLAIMS:

1.   A process for producing a chemical inter-
mediate for polymer manufacture comprising:
          reacting a Schiff's base of formula (III):

          $Ar_1CH=NAr_2$ (III)

with an N-arylmethylheterocycle of formula (IV):

          $Ar_3-CH_2-N\big)$ (IV)

in a basic medium
wherein Ar_1, Ar_2 and Ar_3 are each independently
selected from aryl and hetaryl,   unsubstituted or
substituted, one or more times, by radicals selected
from F, Cl, Br; alkyl of 1 to 6 carbon atoms; alkenyl
of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms;
aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18
carbon atoms, alkoxy of 1 to 6 carbon atoms; thio-
alkoxy of 1 to 6 carbon atoms; aryloxy of 6 to 12
carbon atoms; and thioaryloxy of 6 to 12 carbon
atoms; and

          $-N\big)$

is a hetaryl radical.

2.   A process according to claim 1, including a
step of recovering a diaryl acetylene reaction
product of formula (I):

-37-

$$Ar_1-C\equiv C-Ar_3 \qquad\qquad (I)$$

wherein Ar_1 and Ar_3 are as defined in claim 1.

3.   A process according to claim 2, wherein Ar_1 and Ar_3 are both fluoroaryl.

4.   A process according to claim 3, including a step of converting at least one fluorine substituent of the fluoroaryl radicals Ar_1 and Ar_3 to a hydroxy substituent.

5.   A process according to claim 1, including a step of recovering an enamine of formula (II):

$$Ar_1-CH=\underset{\underset{\displaystyle N}{|}}{C}-Ar_3 \qquad\qquad (II)$$

wherein Ar_1, Ar_3 and N are as defined in claim 1.

6.   A process for producing a diarylacetylene of formula (I):

$$Ar_1-C\equiv C-Ar_3 \qquad\qquad (I)$$

comprising susbjecting an enamine of formula (II):

$$Ar_1-CH=\underset{\underset{\displaystyle N}{|}}{C}-Ar_3 \qquad\qquad (II)$$

to a basic condition effective for elimination of

$$H-N$$

wherein Ar_1 and Ar_3 are each independently selected from aryl and hetaryl, unsubstituted or substituted, one or more times, by radicals selected from F, Cl,

Br;   alkyl of 1 to 6 carbon atoms;   alkenyl of 2 to 6
carbon atoms;   aryl of 6 to 12 carbon atoms;   aralkyl
of 7 to 18 carbon atoms;   aralkenyl of 8 to 18 carbon
atoms, alkoxy of 1 to 6 carbon atoms; thioalkoxy of 1
to 6 carbon atoms;   aryloxy of 6 to 12 carbon atoms;
and thioaryloxy of 6 to 12 carbon atoms; and

$$-N \supset$$

is a pseudohalogen hetaryl radical.

7.   A process according to claim 6, wherein Ar_1
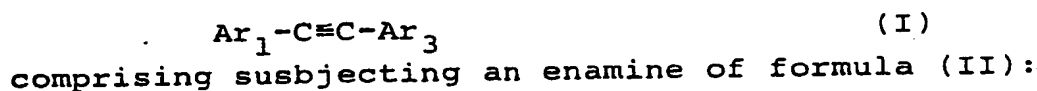and Ar_3 are both fluoroaryl.

8.   A process according to claim 7, including a
step of converting at least one fluorine substituent
of the fluoroaryl radicals Ar_1 and Ar_3 to a hydroxy
substituent.

9.   A process for producing a diarylacetylene
of formula (I):

$$Ar_1 - C \equiv C - Ar_3 \qquad\qquad (I)$$

comprising:
          reacting a Schiff's base of formula (III):

$$Ar_1 CH = NAr_2 \qquad\qquad (III)$$

with an N-arylmethylheterocycle of formula (IV):

$$Ar_3 - CH_2 - N \supset \qquad\qquad (IV)$$

in a basic medium effective for elimination of $H-N \supset$
from an enamine of formula (II):

$$Ar_1-CH=\underset{\underset{N}{|}}{C}-Ar_3 \qquad\qquad (II)$$

wherein Ar_1, Ar_2 and Ar_3 are each independently selected from aryl and hetaryl, unsubstituted or substituted, one or more times, by radicals selected from F, Cl, Br; alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms; thio-alkoxy of 1 to 6 carbon atoms; aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6 to 12 carbon atoms; and

$$-N\rangle$$

is a hetaryl radical that behaves as a pseudohalogen.

10.   A process for producing an enamine of formula (II)

$$Ar_1-CH=\underset{\underset{N}{|}}{C}-Ar_3 \qquad\qquad (II)$$

comprising reacting a Schiff's base of formula (III):

$$Ar_1CH=NAr_2 \qquad\qquad (III)$$

with an N-arylmethylheterocycle of formula (IV):

$$Ar_3-CH_2-N\rangle \qquad\qquad (IV)$$

-40-

in a basic medium ineffective for elimination of

$$H-N)$$

from product. enamine of said formula (II) wherein Ar_1, Ar_2 and Ar_3 are each independently selected from aryl and hetaryl, unsubstituted or substituted, one or more times, by radicals selected from F, Cl, Br; alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms; aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6 to 12 carbon atoms; and -N) is a hetaryl radical.

11.   An enamine of formula (II):

$$Ar_1-CH=C-Ar_3 \qquad\qquad (II)$$
$$\underset{\underset{\sim}{N}}{}$$

wherein Ar_1 and Ar_3 are each independently selected from aryl and hetaryl, unsubstituted or substituted, one or more times, by radicals selected from F, Cl, Br; alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms; aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6 to 12 carbon atoms; and -N) is a hetaryl radical other than imidazolyl.
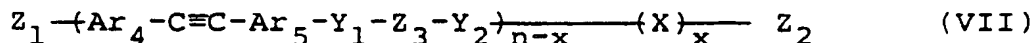
12.   An enamine according to claim 11, wherein said hetaryl -N) is selected from the group consisting of unsubstituted or substituted benzimidazolyl, benzotriazolyl, triazolyl and tetrazolyl.

13.   An enamine according to claim 11, wherein said hetaryl $-N$⟩ is unsubstituted or substituted benzimidazolyl.
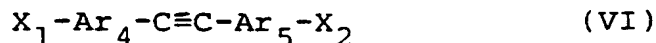
14.   An·enamine according to claim 11, wherein said hetaryl $-N$⟩ is unsubstituted or substituted benzotriazolyl.

15.   A process for producing an acetylenic group-containing polymer or copolymer of formula (VII):

$$Z_1 \text{---}(Ar_4 \text{-} C \equiv C \text{-} Ar_5 \text{-} Y_1 \text{-} Z_3 \text{-} Y_2)_{n-x} \text{---} (X)_x \text{---} Z_2 \qquad (VII)$$

wherein Z_1 is fluorine, hydroxyl or mercaptyl, Z_2 is hydrogen or fluorine, Z_3 is $-O-$, $-S-$, $-CH_2-$, $-CO-$, $-CO-Ar_6-CO-$ or $-Ar_7-$, in which Ar_6 and Ar_7 are selected from divalent aromatic linkages, Y_1 and Y_2 are each selected from $-O-$ and $-S-$, provided that when Z_3 is $-O-$ or $-S-$, Y_1 and Y_2 are both single bonds, Ar_4 and Ar_5 are each independently selected from arylene and hetarylene, unsubstituted or substituted one or more times by radicals selected from F, Cl, Br, alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms, thioalkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 12 carbon atoms and thioaryloxy of 6 to 12 carbon atoms; X is $-Ar_4-C \equiv C-Ar_5$ or a copolymer unit, n is an integer of 2 to 200, x is an integer of 0 to 199 and n is $> x$, comprising:
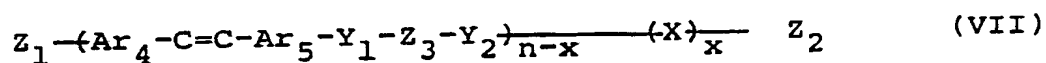
      polymerizing a diarylacetylene of formula (VI):

$$X_1 \text{-} Ar_4 \text{-} C \equiv C \text{-} Ar_5 \text{-} X_2 \qquad (VI)$$

in which X_1 and X_2 are independently selected from F and OH and Ar_4 and Ar_5 are as defined above, or copolymerizing said diarylacetylene of formula (VI) with a comonomer selected from dihydroxy aromatics and dihaloaromatics in which the halogen atoms are activated for displacement, or in the presence of a reactant which provides a divalent linkage for the acetylenic monomer units, selected from $-CH_2-$, $-O-$, $-S-$, $-CO-$ or said copolymer unit X.
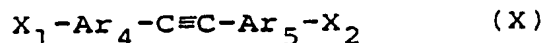
16.   An acetylenic group-containing polymer or copolymer of formula (VII):

$$Z_1-\left(Ar_4-C\!=\!C-Ar_5-Y_1-Z_3-Y_2\right)_{\overline{n-x}}\left(X\right)_{\overline{x}}\; Z_2 \qquad (VII)$$

wherein Z_1 is fluorine, hydroxyl or mercaptyl, Z_2 is hydrogen or fluorine, Z_3 is $-O-$, $-S-$, $-CH_2-$, $-CO-$, $-CO-Ar_6-CO-$ or $-Ar_7-$, in which Ar_6 and Ar_7 are selected from divalent aromatic linkages, Y_1 and Y_2 are each selected from $-O-$ and $-S-$, provided that when Z_3 is $-O-$ or $-S-$, Y_1 and Y_2 are both single bonds, Ar_4 and Ar_5 are each independently selected from arylene and hetarylene, unsubstituted or substituted one or more times by radicals selected from F, Cl, Br, alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms, thioalkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 12 carbon atoms and thioaryloxy of 6 to 12 carbon atoms; X is $-Ar_4-C\!\equiv\!C-Ar_5$ or a copolymer unit, n is an integer of 2 to 200, x is an integer of 0 to 199 and n is vx, provided that when the polymer or copolymer has acetylenic units $-Ar_4-C\!\equiv\!C-Ar_5$ at both terminal positions, n is at least 3.
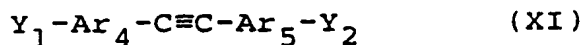
-43-

17.   A process for producing a diaryl actetylene of formula (X)

$$X_1-Ar_4-C\equiv C-Ar_5-X_2 \qquad (X)$$

in which one of X_1 and X_2 is -OR and the other is F or -OR, in which R is alkyl or aryl comprising:

reacting a diarylacetylene of formula (XI):

$$Y_1-Ar_4-C\equiv C-Ar_5-Y_2 \qquad (XI)$$

in which one of Y_1 and Y_2 is F and the other is H or F, with an alkoxide or aryloxide, wherein Ar_4 and Ar_5 are each independently selected from aryl and hetaryl unsubstituted or substituted, one or more times, by radicals selected from F, Cl, Br, alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms; aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6 to 12 carbon atoms.

AMENDED CLAIMS
[received by the International Bureau on 26 March 1993 (26.03.93):
original claims 11 and 12 amended; remaining claims unchanged (4 pages)]

in a basic medium ineffective for elimination of.

$$H-N)$$

from product enamine of said formula (II) wherein Ar_1, Ar_2 and Ar_3 are each independently selected from aryl and hetaryl, unsubstituted or substituted, one or more times, by radicals selected from F, Cl, Br; alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms; aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6 to 12 carbon atoms; and -N) is a hetaryl radical.

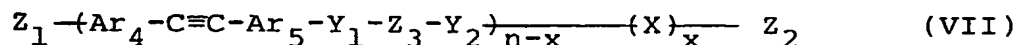11.   An enamine of formula (II):

$$Ar_1-CH=C-Ar_3 \qquad\qquad (II)$$
$$\underset{\underset{\widetilde{N}}{|}}{}$$

wherein Ar_1 and Ar_3 are each independently selected from aryl and hetaryl, unsubstituted or substituted, one or more times, by radicals selected from F, Cl, Br; alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms; aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6 to 12 carbon atoms; and -N) is a hetaryl radical selected from the group consisting of benzimidazolyl and benzotriazolyl, provided that when said hetaryl radical -N) is benzotriazolyl Ar_1 and Ar_3 are each independently selected from said unsubstituted or substituted hetaryl.

12.   An enamine according to claim 11, wherein Ar_1 and Ar_3 are each independently selected from aryl of 6 to 16 carbon atoms and hetaryl selected from the group consisting of pyridinyl, furanyl, thiaphenyl, thiazolyl and quinolinyl, unsubstituted or substituted.

13.   An enamine according to claim 11, wherein said hetaryl -N) is unsubstituted or substituted benzimidazolyl.

14.   An enamine according to claim 11, wherein said hetaryl -N) is unsubstituted or substituted benzotriazolyl.
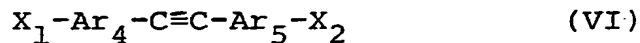
15.   A process for producing an acetylenic group-containing polymer or copolymer of formula (VII):

$$Z_1 + Ar_4 - C \equiv C - Ar_5 - Y_1 - Z_3 - Y_2 \underset{n-x}{\rule[-0.3em]{0pt}{1em}} \quad (X)_x \quad Z_2 \qquad (VII)$$

wherein Z_1 is fluorine, hydroxyl or mercaptyl, Z_2 is hydrogen or fluorine, Z_3 is -O-, -S-, -CH$_2$-, -CO-, -CO-Ar$_6$-CO- or -Ar$_7$-, in which Ar_6 and Ar_7 are selected from divalent aromatic linkages, Y_1 and Y_2 are each selected from -O- and -S-, provided that when Z_3 is -O- or -S-, Y_1 and Y_2 are both single bonds, Ar_4 and Ar_5 are each independently selected from arylene and hetarylene, unsubstituted or substituted one or more times by radicals selected from F, Cl, Br, alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms, thio-alkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 12 carbon atoms and thioaryloxy of 6 to 12 carbon atoms;
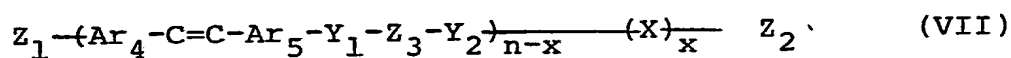
X is $-Ar_4-C≡C-Ar_5$ or a copolymer unit, n is an integer of 2 to 200, x is an integer of 0 to 199 and n is >x, comprising:

polymerizing a diarylacetylene of formula (VI):

$$X_1-Ar_4-C≡C-Ar_5-X_2 \qquad (VI)$$

in which X_1 and X_2 are independently selected from F and OH and Ar_4 and Ar_5 are as defined above, or copolymerizing said diarylacetylene of formula (VI) with a comonomer selected from dihydroxy aromatics and dihaloaromatics in which the halogen atoms are activated for displacement, or in the presence of a reactant which provides a divalent linkage for the acetylenic monomer units, selected from $-CH_2-$, $-O-$, $-S-$, $-CO-$ or said copolymer unit X.
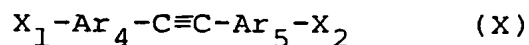
16. An acetylenic group-containing polymer or copolymer of formula (VII):

$$Z_1-(Ar_4-C=C-Ar_5-Y_1-Z_3-Y_2)_{n-x}-(X)_x \quad Z_2 \qquad (VII)$$

wherein Z_1 is fluorine, hydroxyl or mercaptyl, Z_2 is hydrogen or fluorine, Z_3 is $-O-$, $-S-$, $-CH_2-$, $-CO-$, $-CO-Ar_6-CO-$ or $-Ar_7-$, in which Ar_6 and Ar_7 are selected from divalent aromatic linkages, Y_1 and Y_2 are each selected from $-O-$ and $-S-$, provided that when Z_3 is $-O-$ or $-S-$, Y_1 and Y_2 are both single bonds, Ar_4 and Ar_5 are each independently selected from arylene and hetarylene, unsubstituted or substituted one or more times by radicals selected from F, Cl, Br, alkyl of 1 to 6 carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of 6 to 12 carbon atoms; aralkyl of 7 to 18 carbon atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1 to 6 carbon atoms, thio-
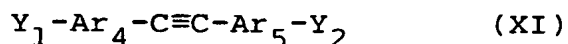
alkoxy of 1 to 6 carbon atoms, aryloxy of 6 to 12
carbon atoms and thioaryloxy of 6 to 12 carbon atoms;
X is $-Ar_4-C{\equiv}C-Ar_5$ or a copolymer unit, n is an
integer of 2 to 200, x is an integer of 0 to 199 and
n is vx, provided that when the polymer or copolymer
has acetylenic units $-Ar_4-C{\equiv}C-Ar_5$ at both terminal
positions, n is at least 3.

17.   A process for producing a diaryl actetylene
of formula (X)

$$X_1-Ar_4-C{\equiv}C-Ar_5-X_2 \qquad (X)$$

in which one of X_1 and X_2 is $-OR$ and the other is F
or $-OR$, in which R is alkyl or aryl comprising:
        reacting a diarylacetylene of formula (XI):

$$Y_1-Ar_4-C{\equiv}C-Ar_5-Y_2 \qquad (XI)$$

in which one of Y_1 and Y_2 is F and the other is H or
F, with an alkoxide or aryloxide, wherein Ar_4 and Ar_5
are each independently selected from aryl and hetaryl
unsubstituted or substituted, one or more times, by
radicals selected from F, Cl, Br, alkyl of 1 to 6
carbon atoms; alkenyl of 2 to 6 carbon atoms; aryl of
6 to 12 carbon atoms; aralkyl of 7 to 18 carbon
atoms; aralkenyl of 8 to 18 carbon atoms, alkoxy of 1
to 6 carbon atoms; thioalkoxy of 1 to 6 carbon atoms;
aryloxy of 6 to 12 carbon atoms; and thioaryloxy of 6
to 12 carbon atoms.

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07C15/54;   C08G65/40;   C07C15/60;   C07D235/06
C07D249/08;   C07D249/18;   C07D307/36;   C07D213/06

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07C ; C08G ; C07D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[o]	Citation of Document, [11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 1 1987, LETCHWORTH GB pages 819 - 823 A.R. KATRITZKY 'The chemistry of N-substituted benzotriazoles. Part 6. A new synthetic route to aromatic ketones' * page 820, compound 11 *	11
P,X	JOURNAL OF THE CHEMICAL SOCIETY, PERKIN TRANSACTIONS 1 7 June 1992, LETCHWORTH GB pages 1295 - 1998 A.R. KATRIZKY ET AL. 'New synthesis of diarylalkynes from 1-(arylmethyl)benzotriazoles and arylideneamines' * step 1a,c + 5; step 12a,c - - 13 *	1,2,5,6, 9-12

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 JANUARY 1993	1 8. 02. 93

International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	VAN BIJLEN H.